

Code No. : 5414

Sub. Code : ZCHM 23

M.Sc. (CBCS) DEGREE EXAMINATION, APRIL 2023.

Second Semester

Chemistry — Core

ELECTROCHEMISTRY AND SPECTROSCOPY — II

(For those who joined in July 2021 onwards)

Time : Three hours

Maximum : 75 marks

PART A — (10 × 1 = 10 marks)

Answer ALL the questions.

Choose the correct answer :

1. For an aqueous solution Debye-Huckel Limiting Law is given by
- (a) $\log \gamma_{\pm} = 0.509 |Z_+ Z_-| \sqrt{\mu}$
 (b) $\log \gamma_{\pm} = 0.509 |Z_+ Z_-| \mu$
 (c) $\log \gamma_{\pm} = -0.509 |Z_+ Z_-| \sqrt{\mu}$
 (d) $\log \gamma_{\pm} = -0.509 |Z_+ Z_-| \mu$

6. Appearance of continuum after progression in electronic spectrum indicates that the _____.
- (a) Dissociation (b) Pre dissociation
 (c) Ionisation (d) None of the above
7. Which of the following systems will not show ESR spectrum?
- (a) Cl^- (b) N_2^-
 (c) NO_2 (d) I_2^-
8. $^3J_{\text{HH}}$ coupling constants depend on
- (a) Magnetic field strength
 (b) Relative orientation of the coupled protons
 (c) Sample concentration
 (d) 90° Pulse width
9. The correct order of the isomeric shift in Mössbauer spectra (^{57}Fe source) of high spin iron compound is
- (a) $\text{Fe(II)} > \text{Fe(III)} > \text{Fe(IV)}$
 (b) $\text{Fe(III)} > \text{Fe(II)} > \text{Fe(IV)}$
 (c) $\text{Fe(IV)} > \text{Fe(III)} > \text{Fe(II)}$
 (d) $\text{Fe(IV)} > \text{Fe(II)} > \text{Fe(III)}$

2. Example of highly non polarisable electrodes
- (a) Glass (b) Calomel
 (c) Mercury (d) Silver
3. Which one of the following conductometric titrations will show a linear increase with volume of the titrant added up to the break point and an almost constant conductance afterwards?
- (a) A strong acid with a strong base
 (b) A strong acid with a weak base
 (c) A weak acid with a strong base
 (d) A weak acid with a weak base
4. The output of a voltammetric analysis of an electroactive analyte is
- (a) Current – Time curve
 (b) Charge – Time curve
 (c) Current – Potential curve
 (d) Charge – Temperature curve
5. UV PES spectrum of a molecule shows a single sharp line. Then the electron is ejected from _____.
- (a) Bonding Molecular Orbital
 (b) Anti-bonding molecular orbital
 (c) Non-bonding orbital
 (d) None of the above

10. NQR spectra is observed in _____ region.
- (a) Microwave (b) Radio frequency
 (c) X-ray (d) UV/Visible

PART B — (5 × 5 = 25 marks)

Answer ALL the questions, choosing either (a) or (b).

Each answer should not exceed 250 words.

11. (a) Discuss the thermodynamic treatment of electrified interface leading to the derivation of Lippmann equation.
- Or
- (b) Explain the following :
- (i) Wein effect
 (ii) Debye-Falkenhagen effect.
12. (a) Discuss the principle and applications of cyclic voltammetry.
- Or
- (b) Calculate the Liquid Junction Potential at 25°C between two solutions of HCl having mean ionic activities of 0.01 and 0.001 respectively. The transference number of H^+ ion (t_+) in HCl may be taken as 0.83.

13. (a) The photoelectron spectrum of O_2 was recorded using the electromagnetic radiation of wavelength 58.43 nm. Two peaks were found with kinetic energies 9.30 eV and 5.20 eV. Calculate the ionisation energies corresponding to these two peaks.

Or

- (b) Discuss the vibrational progression in electronic spectra.
14. (a) How can lines due to spin-spin splitting be differentiated from those of the chemical shift?

Or

- (b) For the following molecules give the number of lines expected in a resolved ESR spectrum
- methyl radical
 - naphthalene anion.
15. (a) With the help of Mössbauer spectra how can you differentiate between $FeSO_4$ and $FeCl_3$?

Or

- (b) Deduce the mass spectral splitting pattern of butanal.

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PART C — (5 × 8 = 40 marks)

Answer ALL the questions, choosing either (a) or (b).

Each answer should not exceed 600 words.

16. (a) Discuss the structure of electrified interface with reference to Helmholtz-Perrin and Gouy-Chapmann theories.

Or

- (b) Derive Debye-Huckel Limiting Law equation. How can it be verified?

17. (a) Discuss the theories of Hydrogen Overvoltage.

Or

- (b) Derive Butler-Volmer equation.

18. (a) Summarize the features of X-ray photoelectron spectroscopy and give its applications.

Or

- (b) Elucidate the fate of electronically excited molecules with reference to dissociation, fluorescence, phosphorescence.

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19. (a) (i) Elucidate the splitting pattern of NMR signal in AMX system.
- (ii) The chemical shift of benzene protons is lower than that of olefinic protons. Why?

Or

- (b) Why does anisotropy occur in g -value of ESR? Discuss anisotropic g factors and its effect in hyperfine splitting.

20. (a) Arrive at the NQR spectral pattern for the following nuclei under the conditions indicated and explain.

(i) $^{127}I: I = 5/2 \quad \eta = 0 \quad B_0 = 0$

(ii) $^{35}Cl: I = 3/2 \quad \eta = 0 \quad B_0 \neq 0$

Or

- (b) (i) What is recoil energy? Discuss its effect and how is it eliminated while recording Mössbauer spectra.

- (ii) Discuss the following :

(i) Molecular ion peak

(ii) Metastable ion.

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